

(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 652 245 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
09.08.2000 Bulletin 2000/32

(51) Int. Cl.⁷: C08G 77/08, C08G 77/18,
C08G 77/14, C08G 77/28,
C08G 77/22, C08G 77/20

(21) Application number: 94117511.9

(22) Date of filing: 07.11.1994

(54) **Process for preparing organic functional group-containing organopolysiloxanes, organopolysiloxanes obtained by the process and mercapto group and alkoxy group-containing organopolysiloxanes and preparation thereof**

Verfahren zur Herstellung von Organo-funktionelle Gruppen enthaltenden Organopolysiloxanen und daraus hergestellte Organopolysiloxane, Mercapto- und Alkoxygruppen enthaltende Organopolysiloxane und Verfahren zu deren Herstellung

Procédé de préparation d'un organopolysiloxane ayant des groupes organiques fonctionnels, polysiloxanes préparés par ce procédé organopolysiloxanes à groupes mercapto et alkoxy et procédé pour leur préparation

(84) Designated Contracting States:
DE FR GB

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(30) Priority: 05.11.1993 JP 27636493
08.11.1993 JP 30240893
03.03.1994 JP 6010694

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(43) Date of publication of application:
10.05.1995 Bulletin 1995/19

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US-A- 5 039 771 US-A- 5 086 145

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• DATABASE WPI Derwent Publications Ltd.,
London, GB; AN 84-221813 & JP-A-59 129 230
(DAINIPPON INK CHEM KK.) , 25 July 1984
• DATABASE WPI Derwent Publications Ltd.,
London, GB; AN 84-191772 & JP-A-59 108 033
(DAINIPPON INK CHEM KK.) , 22 June 1984

EP 0 652 245 B1

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DescriptionBACKGROUND OF THE INVENTION5 **Field of The Invention**

[0001] This invention relates to a process for preparing organic functional group-containing organopolysiloxanes and also to organopolysiloxanes obtained by the process. The invention also relates to a process for preparing a process for preparing organopolysiloxanes having a polymer moiety having specific types of recurring units. The invention 10 relates to a novel organopolysiloxane oligomer or polymer having both a mercapto functional group and an alkoxy group and a process for preparing such a novel oligomer or polymer.

Description of the Related Art

15 [0002] A number of organic functional group-containing organopolysiloxane powder materials have been already proposed including a process wherein tetraalkoxysilanes and organoalkoxysilanes are subjected to co-hydrolysis and polycondensation reaction in the presence of ammonia serving as a catalyst as proposed in Japanese Laid-open Patent Application No.4-114065 and a process wherein the above co-hydrolysis and polycondensation reaction is conducted in the presence of hydrofluoric acid (Japanese Laid-open Patent Application No. 62-166887 and Journal of the 20 Japanese Chemical Society 1983 (11), pp. 1577 to 1588).

[0003] On the other hand, for the preparation of polysilsesquioxane, there are known a number of processes for hydrolyzing and polycondensing alkoxy silanes such as methyltrimethoxysilane. In most cases, acids, bases or silanol group-containing compounds are used as a catalyst for the hydrolysis and polycondensation. For instance, Japanese Laid-open Patent Application No. 60-118715 proposes a process wherein hydrolysis is effected using an acid catalyst 25 and the resultant reaction system is rendered basic, followed by subsequent polycondensation. In Japanese Laid-open Patent Application 61-854, a partially hydrolyzed condensate of trialkoxysilane is provided as a catalyst for hydrolysis and polycondensation reaction.

[0004] As is known in the art, however, the above-stated processes for preparing organic functional group-containing organopolysiloxane powders have problems on (1) uniform dispersion or distribution of the organic functional group 30 in the fine pores of the polysiloxane product, (2) a highly reactive organic functional group being kept as it is during and after the course of the hydrolysis and condensation, (3) porosity, and (4) working properties.

[0005] With respect to the uniform dispersion or distribution (1), it is not possible to uniformly disperse or distribute the organic functional group throughout the inside of the fine pore according to a dry process wherein a silane coupling agent is sprayed over silicon dioxide powder. For the uniform dispersion and distribution, it has been accepted as being 35 better to make use of a wet process using a co-hydrolysis reaction. With respect to (2) above, where organopolysiloxane powder materials having a highly active organic functional group such as, for example, an epoxy group are prepared by use of an acid or alkali catalyst, the organic functional group is attacked with the acid or alkali catalyst and its functionality is lost. As for the porosity of (3), when using a process which requires a long time before gelation, organopolysiloxane powder particles are gradually deposited one on another, so that porous powder particles are unlikely to 40 obtain. In this connection, it is known that when HF is used, gelation can be completed within a very short time. This eventually leads to the formation of a very porous organopolysiloxane powder substance. However, the use of HF has the problem that the working environment has to be severely controlled owing to the danger involved in HF.

[0006] On the other hand, when an alkoxy silane having a highly reactive functional group such as an epoxy group is hydrolyzed and condensed or polycondensed to obtain an epoxy group-containing polysilsesquioxane, the known 45 processes set out hereinbefore have the following drawbacks.

[0007] In reaction systems where an acid or base catalyst is used in large amounts, the epoxy group undergoes the electrophilic action owing to H⁺ or the nucleophilic attack of the base, and is readily ring-opened or polymerized, thus not permitting the epoxy group to be left stably.

[0008] On the other hand, in reaction systems containing an acid or base catalyst having a diluted concentration, the hydrolysis and condensation reaction is unlikely to proceed smoothly. The silanol groups formed by the hydrolysis reaction become stabilized, with the possibility that during a long-term reaction, the acidic silanol group inconveniently serves to ring-open the epoxy group.

[0009] When using an acid or base catalyst, silanol groups which are condensable are left in large amounts after completion of the reaction. This may cause the reaction system to be changed as time passes, resulting, for example, 55 in thickening or gelation of the system.

[0010] Most acidic or basic substances are corrosive in nature. Technical consideration should have been taken into account to prevent reactor materials from being corroded. These acidic and basic substances are not beneficial in view of the safety of the working environment.

[0011] Thus, in prior art processes, it has been difficult to obtain organic functional group-containing polysilsesquioxanes of high quality wherein the functional group is present in the sesquioxane stably without involving any significant change in quality in relation to the time and wherein little problem is involved in operation and safety.

[0012] In addition, if it is intended to leave part of an alkoxy group of organic functional group-containing alkoxy silane starting materials after completion of hydrolysis and condensation in reaction systems using an acid or base catalyst, it is essential to carry out partial hydrolysis while controlling an amount of water to be added. The condensation reaction speed in such reaction systems as set out above is not high even when water is employed in large excess. For the partial hydrolysis, a degree of condensation becomes lower. Thus, it will become difficult to prepare a partially hydrolyzed organopolysiloxane product with a desired degree of polymerization.

10 SUMMARY OF THE INVENTION

[0013] It is therefore an object of the present invention to provide a process for preparing organic functional group-containing organopolysiloxanes which overcomes the problems and drawbacks involved in the prior art processes or techniques using acid or base catalysts and which is simple in procedure.

[0014] It is another object of the invention to provide a process for preparing organic functional group-containing organopolysiloxanes in substantially neutral reaction systems wherein the hydrolysis and (poly)condensation reaction proceeds stably without any danger based on the use of acids or bases in prior art processes.

[0015] It is a further object of the invention to provide a process for preparing organic functional group-containing organopolysiloxanes which cover a wide variety of functional groups and which are obtained in the form of resin powder, polymers and oligomers by proper control of the amount of water to be added for the hydrolysis and (poly) condensation reaction.

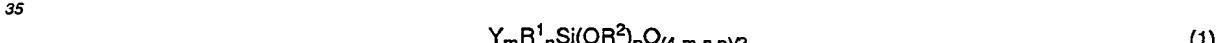
[0016] It is a still further object of the invention to provide a process for preparing organopolysiloxanes having a highly reactive organic functional group therein whereby such polysiloxanes have wide utility in the field of crosslinking agents, reactive coupling agents and reactive diluents.

[0017] It is another object of the invention to provide a process for preparing organopolysiloxanes having a polymer moiety therein whereby good compatibility with various types of synthetic and natural resins or polymers is ensured.

[0018] It is another object of the invention to provide a process for preparing an epoxy group-containing organopolysiloxane.

[0019] It is another object of the invention to provide novel organosiloxane oligomers and polymers having both a mercapto group and at least one alkoxy group and a process for preparing the novel mercapto group and a hydrolyzable group-containing organosiloxane oligomers or polymers.

[0020] According to one embodiment of the invention, there is provided a process for preparing an organic functional group-containing organopolysiloxane of the following average compositional formula (1)



wherein Y represents an organic group having a functional group selected from a substituted or unsubstituted alkenyl group, epoxy group, (meth)acryloxy group, amino group, hydroxyl group, siloxy group, ether group, ketone group and ester group, phosphorus or a polymer moiety comprising aromatic vinyl recurring units, ether recurring units or amide recurring units, R¹ represents at least one monovalent substituted or unsubstituted hydrocarbon group having from 1 to 8 carbon atoms, R² represents at least one member selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms and an alkenyl group having from 2 to 4 carbon atoms, 0<m<1, 0<n<2, and 0<p<2 provided that 0<m+n+p<3, the process comprising providing either an organic functional group-containing alkoxy silane of the following general formula (2)



50 where R¹ and R² have, respectively, the same meanings as defined above, and a is an integer within 0≤a≤2, or a mixture of the organic functional group-containing alkoxy silane of the formula (2) with at least one compound selected from alkoxy silane compounds of the following general formula (3), siloxane compounds of the following general formula (4) and partially and fully hydrolyzed condensates of the alkoxy silane compounds of the formula (3) and/or the siloxane compounds of the formula (4)



wherein R^1 and R^2 have, respectively, the same meanings as defined above b is zero or an integer of 1,2 or 3, c is a value within a range of $0 \leq c \leq 2$, and d is a value within a range of $0 \leq d \leq 3$ provided that $0.01 \leq c+d \leq 3$, and subjecting the organic functional alkoxy silane or the mixture to hydrolysis and polycondensation in the presence of a substantially neutral fluorine-containing compound.

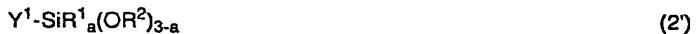
5 [0021] It will be noted that the term "substantially neutral" used herein is intended to mean that the fluorine-containing compound is not exactly neutral in pH but when dissolved in water, the compound is able to release a counter ion other than H^+ relative to F^- , is a neutralized one of HF and may exhibit weak acidity or weak alkalinity.
 [0022] According to another embodiment of the invention, there is also provided a process for preparing a mercapto group-containing organopolysiloxane of the following average compositional formula (1)

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wherein Y^1 represents an organic group having a mercapto group, R^1 represents at least one substituted or unsubstituted monovalent hydrocarbon group having from 1 to 8 carbon atoms, R^2 represents at least one member selected from a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms, and an alkenyl group having from 2 to 4 carbon atoms, $0 < m \leq 1$, $0 \leq n \leq 2$, and $0 \leq p \leq 2$ provided that $0 < m+n+p \leq 3.0$, the process comprising subjecting either a mercapto functional group-containing alkoxy silane of the following general formula (2')

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wherein Y^1 , R^1 and R^2 have, respectively, the same meanings as defined with respect to the formula (1'), a , is an integer of 1, 1 or 3 as defined with respect to the formula (2), or a mixture of the mercapto functional group-containing alkoxy silane of the formula (2') with at least one compound selected from alkoxy silane compounds of the following general formula (3), siloxane compounds of the following general formula (4) and partially and fully hydrolyzed condensates of the alkoxy silane compounds of the formula (3) and/or the siloxane compounds of the formula (4)

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wherein R^1 and R^2 have, respectively, the same meanings as defined above b is zero or an integer of 1, 2 or 3, c is a value within a range of $0 \leq c \leq 2$, and d is a value within a range of $0 \leq d \leq 3$ provided that $0.01 \leq c+d \leq 3$, to hydrolysis and polycondensation in the presence of a substantially neutral fluorine-containing compound.

[0023] In this case, it is preferred that a small amount of an acid or base co-exists with the fluorine-containing compound, unlike the foregoing embodiment in order to facilitate the hydrolysis reaction more efficiently but the acid or base is used in an amount sufficient not to damage the mercapto group.

[0024] The organopolysiloxanes of the formula (1') wherein $0 < m \leq 1$, $0 \leq n \leq 2$, $1 \leq p \leq 2$ provided that $0.1 < m+n+p \leq 3.0$ and thus, the organopolysiloxanes have both a mercapto group and an alkoxy group in the molecule, are not known in the art.

[0025] Such an organopolysiloxane having both a mercapto group and an alkoxy group can be prepared by subjecting a mercapto functional group-containing alkoxy silane of the general formula (2'), or the mixture defined above, to hydrolysis and polycondensation in the presence of a substantially neutral fluorine-containing compound in such a way that water is added to the alkoxy silane or the mixture in an amount less than 1/2 times the total moles of the alkoxy groups present in the alkoxy silane or the mixture.

[0026] In this process, it is also preferred that an acid or base is added along with the substantially neutral fluorine-containing compound to facilitate the hydrolysis and polycondensation reaction using at least the mercapto group-containing alkoxy silane.

BRIEF DESCRIPTION OF THE DRAWINGS

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[0027]

Fig. 1 is a CPMAS (cross polarization magic angle spinning)- ^{13}C -NMR spectrum chart of γ -glycidoxypropyl group-containing organopolysiloxane particles obtained in Example 1;
 Fig. 2 is a CPMAS- ^{13}C -NMR spectrum chart of organopolysiloxane particles obtained in Comparative Example 1;
 Fig. 3 is an FT-IR (Fourier transformation of infrared spectroscopy) chart of vinyl group-containing organopolysiloxane particles obtained in Example 6;
 Fig. 4 is an FT-IR chart of styryl group-containing organopolysiloxane particles obtained in Example 7;

$(\text{NH}_4)_2\text{SiF}_6$.

[0033] These fluorides and fluorine-containing silicon compounds may be used singly or in combination.

[0034] Of these, in view of the cost, solubility in solvent, handling and safety, it is preferred to use NaF , KF , $[(\text{C}_4\text{H}_9)_4\text{N}]^+\text{F}^-$ and Na_2SiF_6 . More preferably, NaF , KF and $[(\text{C}_4\text{H}_9)_4\text{N}]^+\text{F}^-$ are used. Most preferably, KF or $[(\text{C}_4\text{H}_9)_4\text{N}]^+\text{F}^-$ is used.

[0035] The fluorine-containing compound may be directly added to at least one starting material for hydrolysis or after dilution with water or organic solvents. The fluorine-containing compound should preferably be present in a reaction system in such an amount that a molar ratio between the Si atoms present in all starting alkoxy group-containing materials and the F atoms in the fluorine-containing compound used ranges from 1:0.00001 to 1:2, more preferably 1:0.01 to 1:0.1. If the molar ratio of F used is lower than 1:0.00001, the fluorine-containing compound does not serve as a catalyst for the hydrolysis satisfactorily, undesirably taking a very long time for the reaction. In addition, the resultant organopolysiloxane is unlikely to exhibit good properties in most cases. On the other hand, when the molar ratio of F exceeds 2, the pot yield lowers, thus with the great possibility of high production costs.

[0036] In the first embodiment of the invention, there is provided a process for preparing an organic functional group-containing organopolysiloxane of the following average compositional formula (1)



wherein Y represents an organic group having a member selected from the group consisting of a substituted or unsubstituted alkenyl group, epoxy group, (meth)acryloxy group, amino group, hydroxyl group, siloxy group, ether group, ketone group, ester group, phosphorus or a polymer moiety comprising aromatic vinyl recurring units, ether recurring units or amide recurring units, R^1 represents at least one monovalent substituted or unsubstituted hydrocarbon group having from 1 to 8 carbon atoms, R^2 represents at least one member selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms and an alkenyl group having from 2 to 4 carbon atoms, $0 < m \leq 1$, $0 \leq n \leq 2$, and $0 \leq p \leq 2$ provided that $0 < m+n+p \leq 3$, the process comprising providing an organic functional group-containing alkoxy silane of the following general formula (2)



wherein R^1 and R^2 have, respectively, the same meanings as defined above, and a is an integer within $0 \leq a \leq 2$, and subjecting the organic functional alkoxy silane or its mixture with at least one compound selected from alkoxy silane compounds of the following general formula (3), siloxane compounds of the following general formula (4) and partially and fully hydrolyzed condensates of the alkoxy silane compounds of the formula (3) and/or the siloxane compounds of the formula (4)



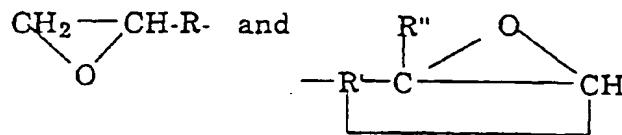
wherein R^1 and R^2 have, respectively, the same meanings as defined above b is zero or an integer of 1, 2 or 3, c is a value within a range of $0 \leq c \leq 2$, and d is a value within a range of $0 \leq d \leq 3$ provided that $0.01 \leq c+d \leq 3$, to hydrolysis and polycondensation in the presence of a substantially neutral fluorine-containing compound.

[0037] The functional group-containing alkoxy silane of the general formula (2) which is an essential starting material in this embodiment of the invention is described in detail.

[0038] The organic group represented by Y in the formulas (1) and (2) should contain a substituted or unsubstituted alkenyl group, epoxy group, (meth)acryloxy group, amino group, hydroxyl group, siloxy group, ether group, ketone group and ester group, phosphorus or a polymer moiety.

[0039] The organic group containing a substituted or unsubstituted alkenyl group includes an ethylene group and those groups represented by the general formula, $\text{CH}_2=\text{CHR}^4-$ wherein R^4 represents a divalent hydrocarbon group with 1 to 10 carbon atoms. Examples of the organic group include $-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2=\text{CH}(\text{CH}_2)_4-$, $\text{CH}_2=\text{CH}(\text{CH}_2)_8-$ and those groups mentioned above but substituted with a halogen such as fluorine or chlorine.

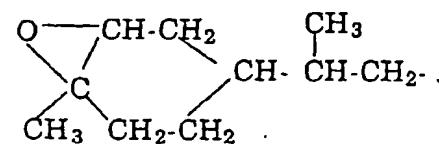
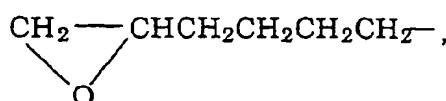
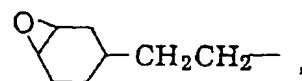
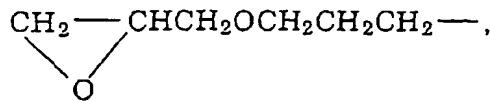
[0040] The epoxy group-containing organic group represented by Y^2 includes those groups of the following general formulas



10 wherein R represents a divalent hydrocarbon group having from 1 to 8 carbon atoms with or without an oxygen atom in the hydrocarbon group, R' represents a trivalent hydrocarbon group having from 6 to 10 carbon atoms, and R" represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or an alkenyl group having from 2 to 4 carbon atoms.

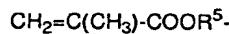
[0041] Specific examples include

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[0042] The (meth)acryloxy group-containing organic group is represented by the following formulas

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50 wherein each R⁵ represents a divalent hydrocarbon group having from 1 to 8 carbon atoms.

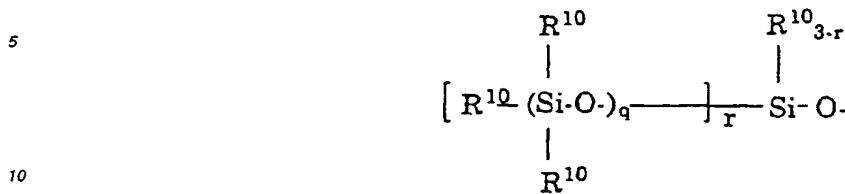
[0043] The amino group-containing organic groups include those groups of the following general formulas of H_2NR^6- , R^7HNR^6- and R^8_2NR^6- wherein R⁶ is a divalent hydrocarbon group having from 1 to 10 carbon atoms which may have a NH bond therein, and R⁷ and R⁸ are, respectively, an alkyl group having from 1 to 10 carbon atoms, a phenyl group or a benzyl group.

55 [0044] Specific examples of the amino group-containing organic group include $\text{H}_2\text{N}(\text{CH}_2)_3-$, $\text{C}_6\text{H}_5\text{NH}(\text{CH}_2)_3-$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}(\text{CH}_2)_3-$, $\text{CH}_3\text{NH}(\text{CH}_2)_3-$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3-$, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}(\text{CH}_2)_3-$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NHCH}_2\text{C}_6\text{H}_4\text{-(CH}_2)_2-$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3-$, $\text{H}_2\text{N-C}_6\text{H}_4-$, $-(\text{CH}_2)_{10}\text{-NH}_2$ and $-(\text{CH}_2)_3\text{-N}(\text{CH}_3)_2$.

[0045] The hydroxyl group-containing organic group is represented by the formula of $-\text{R}^9\text{-OH}$ wherein R⁹ is an

alkylene group having from 3 to 10 carbon atoms.

[0046] The siloxy group-containing organic group is represented by the following general formula

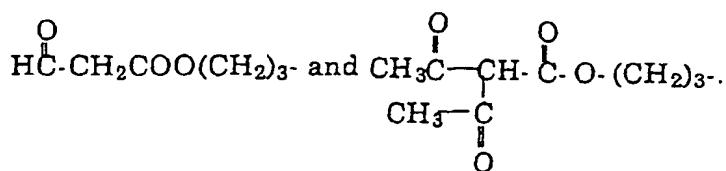


wherein R^{10} represents a hydrogen atom or an alkyl or alkoxy group having from 1 to 10 carbon atoms, an alkenyl group having from 2 to 10 carbon atoms, or a phenyl group, q is zero or an integer of from 1 to 100, and r is 0, 1, 2 or 3.

15 [0047] Specific examples include $(CH_3)_3SiO^-$, $(CH_3)_2SiO$, $CH_2=CH-(CH_3)_2SiO^-$, $C_6H_5(CH_3)_2SiO^-$, $(CH_3)_3Si-[O(CH_3)_2OSi]_{10}-O^-$ and $(CH_3O)_3Si-[O(CH_3)_2Si]_{20}-O^-$.

[0048] The ether group-containing organic group is represented by the general formula of $R^{11}-O-R^{12}-$ wherein R^{11} represents an alkyl group having from 1 to 10 carbon atoms or an alkenyl group having from 2 to 10 carbon atoms, and R^{12} represents an alkylene group having at least one ether bond and having 2 to 10 carbon atoms. Specific examples include $CH_2=CH-CH_2-O-CH_2CH_2-O-(CH_2)_3-$ and $CH_2=C(CH_3)-O-CH_2CH_2-O-(CH_2)_3-$.

20 [0049] The ketone bond-containing organic group is represented by the general formula of $R^{13}C(O)CR^{14}-$ wherein R^{13} represents a hydrogen atom or an alkyl group having from 1 to 10 carbon atoms, and R^{14} represents an alkylene group which may contain a carboxylic acid residue and having from 2 to 10 carbon atoms. Specific examples include

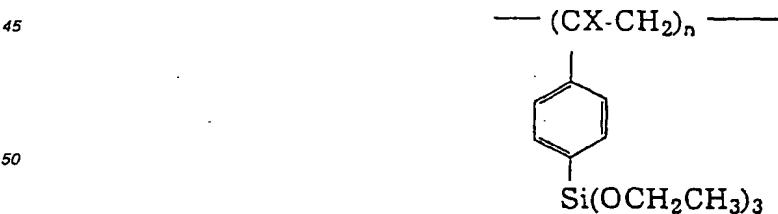


[0050] The ester group-containing organic group is represented by the general formula of $R^{15}COO-$ wherein R^{15} represents an alkyl group having from 1 to 18 carbon atoms and an alkenyl group having 2 to 18 carbon atoms with or without a divalent hydrocarbon group having from 1 to 10 carbon atoms and bonded to the oxygen. Specific examples include $C_{17}H_{35}COO-(CH_2)_3-$ and $CH_2=CHC_{15}H_{30}COO-(CH_2)_3-$.

35 [0051] The phosphorus-containing organic group is represented by $(R^{16})_2P(CH_2)_n-$ where each R^{16} represents a saturated or unsaturated monovalent hydrocarbon group having from 1 to 6 carbon atoms and n is an integer of from 1 to 10.

[0052] The polymer moiety has aromatic vinyl recurring units, ether recurring units or amide recurring units.

[0053] The aromatic vinyl recurring units-bearing organic group is represented by the following general formula



55 wherein X represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or an alkenyl group having from 2 to 4 carbon atoms, and n is an integer of from 10 to 100.

[0054] The ether recurring units-bearing organic group has the following general formula

-(C_mH_{2m}O)_n-

wherein m is 1, 2, 3 or 4 and n is an integer of 2 to 1.0×10^3 .

5 [0055] The amide recurring units-bearing organic group is represented by capramide recurring units, hexamethyl-adipamide recurring units, hexamethylsebacamide recurring units and ω -aminononai acid recurring units.

[0056] These polymer moieties are incorporated in order to improve miscibility with other synthetic and natural resins, like phenyl group, and the miscibility is improved over that using the phenyl group.

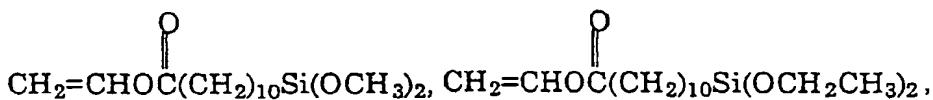
10 [0057] In the formulas (1) and (2), R¹ represents a substituted or unsubstituted monovalent hydrocarbon group having from 1 to 8 carbon atoms. Specific and preferred examples include -CH₃, -CH₂CH₃, -CH₂CH₂CH₃, -CH(CH₃)₂, -CH₂CH₂CH₂CH₃, -CH(CH₃)CH₂CH₃, -C(CH₃)₃, -(CH₃)₂-CH₂-CH₃, -C₆H₅, and those groups mentioned above and substituted with a halogen atom such as fluorine or chlorine.

15 [0058] R² represents a hydrogen atom, a lower alkyl group having from 1 to 4 carbon atoms and a lower alkenyl group having from 2 to 4 carbon atoms. Specific examples of the group represented by R² include -H, -CH₃, -CH₂CH₃, -CH₂CH₂CH₃, -CH(CH₃)₂, -CH₂CH₂CH₂CH₃, -CH(CH₃)CH₂CH₃, -CH₂CH(CH₃)CH₃, -C(CH₃)₃, -CH=CH₂, -CH₂CH=CH₂ and -C(CH₃)=CH₂.

20 [0059] In the general formula (2), a is 0, 1 or 2.

25 [0060] Specific examples of the functional group-containing compounds are mentioned below: CH₂=CHSi(OCH₃)₃, CH₂=CHSi(CH₃)(OCH₃)₂, CH₂=CHSi(OCH₂CH₃)₃, CH₂=CHCH₂Si(OCH₃)₂, CH₂=CHCH₂Si(CH₃)(OCH₃)₂, CH₂=CHCH₂Si(OCH₂CH₃)₂, CH₂=CH(CH₂)₄Si(OCH₃)₂, CH₂=CH(CH₂)₄Si(CH₃)(OCH₃)₂, CH₂=CH(CH₂)₈Si(OCH₂CH₃)₃, CH₂=CHO(CH₂)₃Si(OCH₃)₃ and CH₂=CHO(CH₂)₃Si(OCH₂CH₃)₃;

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30 CH₂=CHC₆H₄Si(OCH₃)₃, and CH₂=CHC₆H₄Si(OCH₂CH₃)₃;

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$$\text{CH}_2-\text{CH}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3)\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3$$

$$\text{CH}_2-\text{CH}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3)-\text{CH}_2$$

$$\text{CH}_2-\text{CH}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiCH}_3(\text{OCH}_3)_2)\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiCH}_3(\text{OCH}_3)_2$$

$$\text{CH}_2-\text{CH}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiCH}_3)(\text{OCH}_2\text{CH}_3)_2$$

$$\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$$

$$\text{O} \text{---} \text{C}_6\text{H}_{11} \text{---} \text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3.$$

$$\text{O} \text{---} \text{C}_6\text{H}_{11} \text{---} \text{CH}_2\text{CH}_2\text{SiCH}_3(\text{OCH}_3)_2.$$

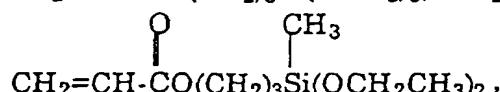
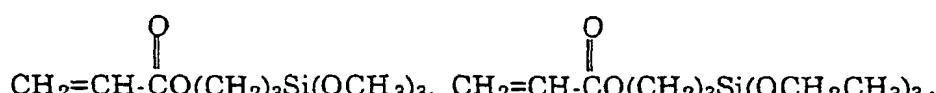
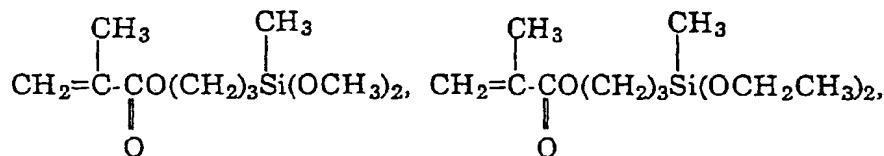
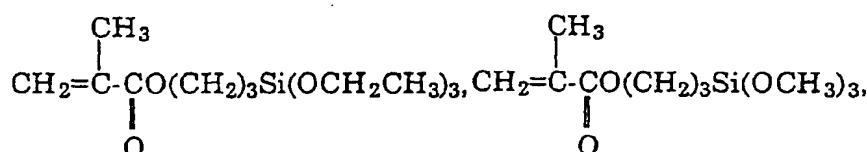
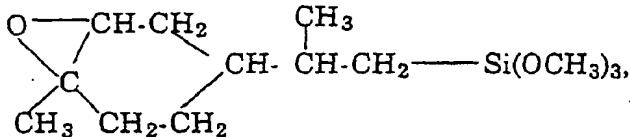
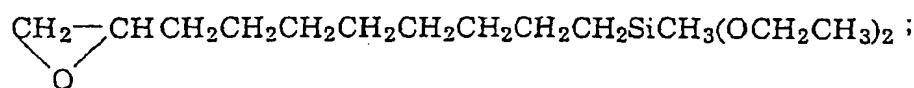
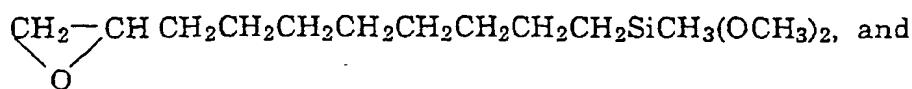
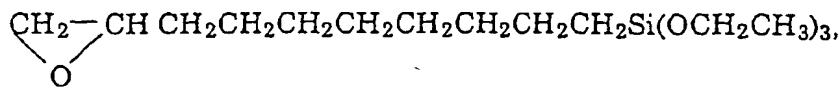
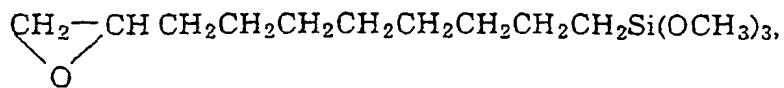
$$\text{CH}_2\text{CH}_2\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2,$$

$$\text{CH}_2-\text{CH}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3,$$

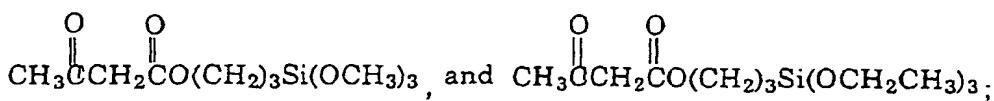
$$\text{CH}_2-\text{CH}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$$

$$\text{CH}_2-\text{CH}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCH}_3(\text{OCH}_3)_2$$

$$\text{CH}_2-\text{CH}(\text{OCH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2,$$

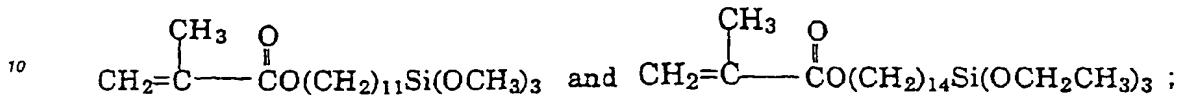


50 $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$,



$(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, and $(\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, and $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$

$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$; $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$,
 $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OCH}_2\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$,
 $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NHCH}_2\text{C}_6\text{H}_5\text{-(CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NHCH}_2\text{C}_6\text{H}_5\text{-(CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$,
 $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$,
 $\text{H}_2\text{N-C}_6\text{H}_5\text{-Si}(\text{OCH}_3)_3$, and $\text{H}_2\text{N-C}_6\text{H}_5\text{-Si}(\text{OCH}_2\text{CH}_3)_3$; $\text{CH}_2=\text{C}(\text{CH}_3)\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ and
 $\text{CH}_2=\text{C}(\text{CH}_3)\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$;



15 H₂N(CH₂)₃Si(OCH₃)₃, H₂N(CH₂)₃Si(OCH₂CH₃)₃, H₂N(CH₂)₃Si(CH₃)(OCH₃)₂, H₂N(CH₂)₃Si(CH₃)(OCH₂CH₃)₂,
C₆H₅NH(CH₂)₃Si(OCH₃), C₆H₅NH(CH₂)₃Si(OCH₂CH₃), C₆H₅CH₂NH(CH₂)₃Si(OCH₃) and
C₆H₅CH₂NH(CH₂)₃Si(OCH₂CH₃); CH₃NH(CH₂)₃Si(OCH₃)₃ and CH₃NH(CH₂)₃Si(OCH₂CH₃)₃;
(CH₃O)₃Si(CH₂)₃NH(CH₂)₂NH(CH₂)₃Si(OCH₃); CH₃CH₂O)₃Si(CH₂)₃NH(CH₂)₂NH(CH₂)₃SiOCH₂CH₃;
(CH₃O)₃Si(CH₂)₃NH(CH₂)₃Si(OCH₃) and (CH₃CH₂O)₃Si(CH₂)₃NH(CH₂)₃Si(OCH₂CH₃); and [(CH₃)₃SiO]-Si(OCH₃)₃,
[(CH₃)₃SiO]₂-Si(OCH₃)₂, [(CH₃)₃SiO]₃-SiOCH₃, [(CH₃)₃SiO]-Si(OCH₂CH₃)₃, [(CH₃)₃SiO]₂-Si(OCH₂CH₃)₃ and
20 [(CH₃)₃SiO]₃-SiOCH₂CH₃.

[0061] The organic functional group-containing alkoxysilanes which are mono, di and tri alkoxysilanes may be used singly or in combination. Accordingly, when used in combination, the alkoxysilanes used should preferably have the same organic functional group but may have different groups represented by R^1 and R^2 in the formula (2). Accordingly, R^1 and R^2 in the formula (1) may, respectively, have different types of groups derived from the different groups represented by R^1 and R^2 in the formula (2).

[0062] The organic functional group-containing groups represented by Y serve as a reactive group in final organopolysiloxanes.

[0063] Of the organic functional groups, an epoxy or (meth)acryloxy group-bearing group is preferred because of its high reactivity. Especially, preferable epoxy group-containing compounds include γ -glycidoxypropyltrimethoxysilane,

30 γ -glycidoxypropylmethyldimethoxysilane, 2-[3,4-epoxycyclohexyl]ethylmethyldimethoxysilane and 2-[3,4-epoxycyclohexyl]ethyltrimethoxysilane. Preferable (meth)acryloxy-group-containing compounds include γ -methacryloxypropyltrimethoxysilane, γ -acryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane and γ -acryloxypropylmethyldimethoxysilane.

[0064] In the practice of the invention, when the organic functional group-bearing alkoxysilane is subjected to hydrolysis and polycondensation reaction in the presence of a substantially neutral fluorine-containing compound as a catalyst, the organic functional group-containing organopolysiloxane of the average compositional formula (1) can be obtained.

[0065] In order to further modify the organopolysiloxanes to impart desired properties different from those of organopolysiloxanes derived from the functional group-containing alkoxysilane alone of the general formula (2), organic functional group-free alkoxysilanes, siloxanes and/or silicones obtained from these alkoxysilanes and siloxanes can be used.

[0066] The organic functional group-free, alkoxy silanes and siloxanes are of the following formulas (3) and (4), respectively



50 wherein R^1 and R^2 have, respectively, the same meaning as defined hereinbefore with respect to the formulas (1) and (2), b is zero or an integer of 1,2 or 3, c is a value within a range of $0 \leq c \leq 2$, d is a value within a range of $0 \leq d \leq 3$ provided that $0.01 \leq c+d \leq 3$.

[0067] The alkoxysilane of the general formula (3) includes a mono, di, tri or tetraalkoxysilane. These alkoxysilanes may be used singly or in combination depending on the purpose as will be described hereinafter. The groups represented by R^1 and R^2 are those described with respect to the formulas (1) and (2) and are not set out herein.

55 [0068] Specific examples of the alkoxysilanes of the general formula (3) are shown below.

Tetra and tri alkoxy silanes:

5 [0069] $\text{Si(OCH}_3)_4$, $\text{Si(OCH}_2\text{CH}_3)_4$, $\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_4$, $\text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$, $\text{CH}_3\text{Si(OCH}_3)_3$,
 $\text{CH}_3\text{Si(OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_3$, $\text{CH}_3\text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$, $\text{CH}_3\text{Si(OCH(CH}_3)=\text{CH}_2)_3$,
 $\text{CH}_3\text{CH}_2\text{Si(OCH}_3)_3$, $\text{CH}_3\text{CH}_2\text{Si(OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{CH}_2\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_3$, $\text{CH}_3\text{CH}_2\text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$,
 $\text{CH}_3\text{CH}_2\text{Si(OC(CH}_3)=\text{CH}_2)_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_3$,
 $\text{CH}_3(\text{CH}_2)_5\text{Si(OCH}_3)_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$, $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Si(OC(CH}_3)=\text{CH}_2)_3$,
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_3)_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_3$,
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OC(CH}_3)=\text{CH}_2)_3$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3$,
 $\text{A-Si(OCH}_3)_3$, $\text{A-Si(OCH}_2\text{CH}_3)_3$, $\text{A-Si(OCH}_2\text{CH}_2\text{CH}_3)_3$, $\text{A-Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$, $\text{A-Si(OC(CH}_3)=\text{CH}_2)_3$, and $\text{A-CH}_2\text{CH}_2\text{Si(OCH}_3)_3$ wherein A represents phenyl.

Dialkoxy silanes:

15 [0070] $(\text{CH}_3)_2\text{Si(OCH}_3)_2$, $(\text{CH}_3)_2\text{Si(OCH}_2\text{CH}_3)_2$, $(\text{CH}_3)_2\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_2$, $(\text{CH}_3)_2\text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$,
 $(\text{CH}_3)_2\text{Si(OC(CH}_3)=\text{CH}_2)_2$, $(\text{CH}_3\text{CH}_2)_2\text{Si(OCH}_3)_2$, $(\text{CH}_3\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_3)_2$, $(\text{CH}_3\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_2$,
 $(\text{CH}_3\text{CH}_2)_2\text{Si(OC(CH}_3)=\text{CH}_2)_2$, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_2$, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Si(OCH}_3)_2$,
 $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_3)_2$, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Si(OC(CH}_3)=\text{CH}_2)_2$,
 $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{Si(OCH}_3)_2$, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_3)_2$, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_2$,
 $\text{20 } (\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{Si(OC(CH}_3)=\text{CH}_2)_2$, $\text{A}_2\text{-Si(OCH}_3)_2$, $\text{A}_2\text{-Si(OCH}_2\text{CH}_3)_2$, $\text{A}_2\text{-Si(OCH}_2\text{CH}_2\text{CH}_3)_2$, $\text{A}_2\text{-Si(OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$, $\text{A}_2\text{-Si(OC(CH}_3)=\text{CH}_2)_2$, and $\text{A}_2\text{-Si(CH}_3)(\text{OCH}_3)_2$ wherein each A represents phenyl.

Monoalkoxy silanes:

25 [0071] $(\text{CH}_3)\text{SiOCH}_3$, $(\text{CH}_3)\text{SiOCH}_2\text{CH}_3$, $(\text{CH}_3)\text{SiOCH}_2\text{CH}_2\text{CH}_3$, $(\text{CH}_3)\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$,
 $(\text{CH}_3)\text{SiOC(CH}_3)=\text{CH}_2$, $(\text{CH}_3)_3\text{SiOH}$, $(\text{CH}_3\text{CH}_2)_3\text{SiOCH}_3$ and $(\text{CH}_3\text{CH}_2)_3\text{SiOCH}_2\text{CH}_3$.
[0072] Examples of the organosiloxanes of the general formula (4) are those shown below.

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hydrolysis) and polycondensation is usually effected at a temperature ranging from 0°C to 100°C, preferably from 20°C to 80°C. It will be noted that when water and a fluorine-containing compound are added to the starting material, the temperature of the reaction system increases but not exceeding the above temperature range. The hydrolysis and polycondensation is usually carried out under agitation, under which the reaction system is kept for aging for a time of 0.1 to 10 hours.

[0080] The catalyst of the substantially neutral fluorine-containing compound used in the present invention remarkably promote the hydrolysis and polycondensation reaction owing to its high catalytic activity. By this, water added to the hydrolysis is completely consumed with little alkoxy groups being left in the final polycondensate, thereby ensuring an organopolysiloxane which has such a structure or form as initially designed. In addition, unlike the hydrolysis using acid or base catalysts, the organic functional groups of the organic functional group-containing silane of the formula (2) other than the alkoxy group are scarcely impeded. It will be noted that although OH groups may be left on in very small amounts, the OH group can be removed by reaction of monoalkoxysilanes, if desired, as will be described hereinafter.

[0081] After completion of the reaction, the catalyst used is removed from the reaction system. To this end, the catalyst may be removed by filtration after distillation of alcohol by-products or after changing with a more hydrophobic organic solvent, followed by washing with water. A small amount of moisture left in the product may be removed by any known procedures including a procedure using a drying agent and an azeotropic dehydration procedure wherein the solvent used is evaporated off.

[0082] By the above procedure, the organic functional group-containing organopolysiloxane of the average compositional formula (1) is obtained.

[0083] The degree of polymerization of the organopolysiloxane is determined mainly by an amount of water used for the hydrolysis. Moreover, the form of the final organopolysiloxane, i.e. solid or liquid, is also determined depending on not only the amount of water used, but also the alkoxy functionality, i.e. the number of alkoxy groups, in a starting material and the amount of the catalyst.

[0084] With respect to the degree of polymerization, when a starting alkoxy silane used is, for instance, a monomer having one silicon atom from which there is obtained, from one mole of the starting alkoxy silane, an organic functional group-containing organopolysiloxane which consists of Z silicon atoms, it is sufficient to use $(Z-1)/Z$ moles of water at the time of the hydrolysis reaction. If water is used in an amount of 1 mole or over or in an amount equimolar to or greater than that of the starting alkoxy silane, the resultant organopolysiloxane tends to have a branched structure. The use of too great an amount of water may result in a powdery or bulky resin material although depending on the type of starting material and the amount of solvent.

[0085] In the process of the invention, organic solvents may be used in the reaction system. Such solvents include, for example, alcohols, ethers, esters and ketones. Specific examples include alcohols such as methyl alcohol, ethyl alcohol, 1-propyl alcohol and 2-propyl alcohol, ethers such as diethyl ether and dipropyl ether, esters such as methyl acetate, ethyl acetate and ethyl acetoacetate, and ketones such as acetone, diethyl ketone, methyl ethyl ketone and methyl isobutyl ketone. These solvents may be used in combination with non-polar solvents such as hexane, benzene, toluene and xylene. If used, alcohols such as methyl alcohol and ethyl alcohol are preferred.

[0086] The amount of the solvent is from 0 to 1000 parts by weight, preferably from 20 to 500 parts by weight, per 100 parts by weight of the starting material. If the amount exceeds 1000 parts by weight, a reaction apparatus has to be made large in size and the pot yield lowers, with poor economy. If the amount of the solvent is less than 20 parts by weight, a homogeneous reaction system may not be attained in some cases. In this sense, the use of the solvent is preferred.

[0087] In practice, it is preferred to drop a predetermined amount of water or an organic solvent diluted with water in a mixed system of a starting monomer material, a fluorine-containing compound catalyst and, optionally, an organic solvent. The catalyst may be added to water or the water-diluted organic solvent. It will be noted that if the mixed system is added to water or the water-diluted solvent, the reaction system is apt to gel and is not thus favorable.

[0088] The amount of water used for the hydrolysis should be not larger than 50 times by mole of all the alkoxy groups in a starting material. If the amount of water exceeds 50 times by mole, the pot yield lowers with poor economy. Within a range of 1/2 to 50 times by mole, the alkoxy groups in the starting material are fully hydrolyzed and substantially disappear. In some case, a small amount of OH groups may be left.

[0089] In order to minimize or fully eliminate the OH group being left, a monoalkoxysilane as set out with respect to the alkoxy silane of the formula (3) is added to the reaction system during the course of or after completion of the hydrolysis, followed by polycondensation. By this, if left, the OH group is silylated and little or no OH group is left in a final organopolysiloxane product. To this end, the monoalkoxysilane is added to a starting material. The amount of the monoalkoxysilane is not critical and is preferably at a molar ratio of the monoalkoxysilane and the organic functional group-containing alkoxy silane of the formula (2) or its mixture with a di or higher polyalkoxysilane of the formula (3), an organosiloxane of the formula (4) and/or the silicone derived therefrom of 0.01:3 to 1:3, more preferably from 0.1:1 to 1:1.

[0090] If the amount of water is less than 1/2 times by mole of the alkoxy groups in the starting material, the alkoxy

group is invariably left in a final product.

[0091] As stated hereinbefore, the degree of polymerization is determined mainly by the amount of water. The control in amount of water enables one to cover a wide variety of products including a dimer having two Si atoms and resins having about 10,000 Si atoms. The liquid oligomers, liquid polymers, solid but bulky polymers and resin particles can

5 be prepared according to the process of the invention. The conditions for the respective forms of the organopolysiloxanes are described.

[0092] When using a starting material which comprises the organic functional group-containing alkoxy silane of the formula (2) and, optionally, the alkoxy silane of the formula (3), the alkoxy siloxane of the formula (4) and/or the silicone derived from the alkoxy silane of the formula (3) and the alkoxy siloxane of the formula (4), the hydrolysis and polycondensation reactions are carried out in the presence of a substantially neutral fluorine-containing compound in such a way that water is added to in a controlled amount of within a range of less than 1/2 times by mole of the total moles of the alkoxy groups in the starting material. There are obtained dimers to polymers having approximately 10,000 Si atoms which have, in the molecule, both the organic functional group and the alkoxy group or groups derived from the compound of the formula (2) and/or the compounds of the formulas (3) and (4) and/or the silicone. More particularly, 10 only by properly controlling the amount of water being added, oligomers and polymers having different degrees of polymerization can be readily obtained. The fluorine-containing compound ensures a very sharp distribution in degree of polymerization, so that a relatively high yield of an intended oligomer or polymer can be attained. In the practice of the invention, it is not essentially required to individually obtain, for example, a dimer or a trimer but to obtain an oligomer or polymer having a major proportion of an intended degree of polymerization.

15 [0093] The oligomers having up to about ten Si atoms are effective for use as a crosslinking agent, a modifier, such as a kind of silane coupling agent, for synthetic or natural resins and a reactive diluent. The polymers may also be used for adhesive materials, coating materials and sealants.

[0094] For a low degree of polymerization or oligomerization, p should have a value within $1 \leq p \leq 2$. This value of p can be readily attained by controlling the amount of water as will be seen in examples appearing hereinafter.

20 [0095] As defined hereinbefore, if used in combination, the alkoxy silane of the formula (3), the alkoxy siloxane of the formula (4) and/or the silicone derived therefrom may be used in an amount up to 99.9 wt%.

[0096] The oligomer and polymer prepared in this manner may have linear, branched, cyclic or mixed structures thereof.

[0097] When using water in an amount of 1/2 to 50 times by mole relative to the total alkoxy groups in starting material, oligomers or polymers having an alkoxy group left therein cannot be obtained. However, only a slight amount of OH group may be, in some cases, left.

25 [0098] According to the process of the invention which makes use of a highly active, substantially neutral fluorine-containing compound as a catalyst, when the silane of the formula (2) is subjected to hydrolysis and polycondensation using water in such an amount as set out above, a viscous liquid substance is obtained although depending on the number of the alkoxy groups in the starting silane and the amount of water within the above-defined range. In the practice of the invention, it is preferred that when measured at 25°C by use of an ordinary rotaviscorometer, the resultant liquid substance has a viscosity in the range of 0.01 to 100 Pas (10 cps., to 100,000 cps), more preferably from 0.1 to 10 Pas (100 cps to 10,000 cps).

30 [0099] In order to improve miscibility with other types of resins, the oligomer, and polymer obtained by the process of the invention should preferably be prepared using an organic functional group-containing and/or an organic functional group-free alkoxy silane having a phenyl group in the molecule singly or in combination with other starting materials. By the incorporation of the phenyl group in final products, the miscibility with other resins improved along with an improved refractive index. The phenyl group-bearing alkoxy silanes are those indicated hereinbefore. The molar ratio of the phenyl group and Si in the starting material is preferably 0.01:1 to 0.9:1. If the phenyl group exceeds 0.9, a liquid substance

35 may not be obtained. More preferably, a molar ratio of the phenyl group and Si is 0.3:1 to 0.7:1.

[0100] If at least 70 wt% of tri, tetra and/or higher polyalkoxy silane (whichever organic functional group-containing or free alkoxy silane) and/or siloxane and/or silicone are used and water is added in large excess, say, 1 to 50 times by mole larger than the total alkoxy groups in the starting material, solid particles which are individually porous and fine are obtained. If the amount of water is less than the above range and/or mono and/or di alkoxy silanes are present in

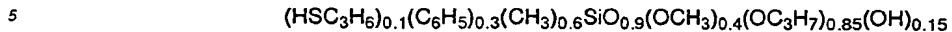
40 larger amounts, viscous polymers or bulky mass of the organopolysiloxane may be obtained.

[0101] It should be noted that the form of the final product is greatly influenced by the amount of water and the alkoxy functionality in a starting material but the amount of water, the alkoxy functionality, the amount of the catalyst and reaction temperature are, more or less, interrelated with one another. The minor difference in these factors may result in a difference in form of a final product.

45 [0102] Solid particles have wide utility in the field of fillers for column, carriers for various types of enzymes and metallic compounds because of their porosity.

[0103] Another embodiment concerning the preparation of mercapto group-containing organopolysiloxane is described.

insoluble matter content of 69.5%, a viscosity of 14 mPas (14.5 cps) (25°C), a specific gravity of 1.089 (25°C), a refractive index of 1.4530 (25°C), a SH content of 2.5 wt% (theoretical: 2.3 wt%) and a S content of 2.2 wt%. The silicone was subjected to analysis of ¹H-NMR, revealing that it was identified as having the following average compositional formula



[0229] The above formula was supported by the results of analyses of ²⁹Si-NMR and IR absorption spectra. The IR spectrum chart is shown in Fig. 17.

10 Example 29

Preparation of $[(HSC_3H_6)_{0.167}(CH_3)_{0.833}SiO_{0.967}(OCH_3)_{1.067}]_{30}$

[0230] The general procedure of Example 25 was repeated using 104.4 g of a 0.1N hydrochloric acid aqueous solution (water: 5.98 mols and HCl: 10.4×10^{-3} mols), thereby obtaining 505.7 g of a silicone resin having a degree of polymerization of 30 at a yield of 83.0%. The resin had an insoluble matter content of 85.2%, a viscosity of 215 mm²/s (215 centistokes) (25°C), a specific gravity of 1.141 (25°C), a SH content of 5.5 wt% (theoretical: 5.4 wt%) and an S content of 5.4 wt%.

20 Example 30

[0231] The general procedure of Example 25 was repeated except that water was used instead of the 0.1 N hydrochloric acid aqueous solution, thereby obtaining 520.2 g of a silicone resin at a yield of 80.5 %. The resin had an insoluble matter content of 76.2%, a viscosity of 12.1 mm²/s (12.1 centistokes) (25°C), a specific gravity of 1.132 (25°C), a SH content of 5.4 wt% (theoretical: 5.4 wt%) and an S content of 5.6 wt%.

Claims

1. A process for preparing an organic functional group-containing organopolysiloxane of the following average compositional formula (1)



wherein Y represents an organic group having a member selected from substituted or unsubstituted alkenyl group, 35 epoxy group, (meth)acryloxy group, amino group, hydroxyl group, siloxy group, ether group, ketone group, ester group, phosphorus or a polymer moiety comprising aromatic vinyl recurring units, ether recurring units or amide recurring units, R¹ represents at least one monovalent substituted or unsubstituted hydrocarbon group having from 1 to 8 carbon atoms, R² represents at least one member selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms and an alkenyl group having from 2 to 4 carbon atoms, 0<m≤1, 40 0≤n≤2, and 0≤p≤2 provided that 0<m+n+p≤3, the process comprising providing either an organic functional group-containing alkoxsilane of the following general formula (2)



45 wherein Y, R¹ and R² have, respectively, the same meanings as defined above, and a is an integer within 0≤a≤2, or a mixture of the organic functional group-containing alkoxsilane of the formula (2) with at least one compound selected from alkoxsilane compounds of the following general formula (3), siloxane compounds of the following general formula (4) and partially and fully hydrolyzed condensates of the alkoxsilane compounds of the formula (3) and/or the siloxane compounds of the formula (4)



55 wherein R¹ and R² have, respectively, the same meanings as defined above, b is zero or an integer of 1,2 or 3, c is a value within a range of 0≤c≤2 and d is a positive value within a range of 0≤d≤3 provided that 0.01≤c+d≤3, and subjecting the organic functional alkoxsilane or the mixture to hydrolysis and polycondensation in the presence of a substantially neutral fluorine-containing compound.

2. A process according to Claim 1, wherein said substantially neutral fluorine-containing compound consists of a fluoride or a compound having at least one Si-F bond in the molecule.

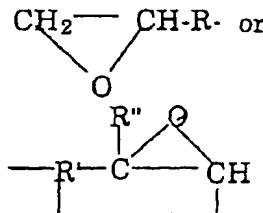
3. A process according to Claim 1 or 2, wherein said substantially neutral fluorine compound is present at a molar ratio between Si atoms in said organic functional group-containing alkoxy silane and the F atoms in said fluorine-containing compound of 1:0.0000 1 to 1:2.

4. A process according to any of the preceding claims, wherein said organic group represented by Y consists of an organic group having a (meth)acryloxy group represented by the general formula



15 wherein each R^5 represents a divalent hydrocarbon group having from 1 to 8 carbon atoms.

5. A process according to any of the preceding claims, wherein said organic group represented by Y consists of an organic group having an epoxy group represented by the general formula



25 30 wherein R represents a divalent hydrocarbon group having from 1 to 8 carbon atoms with or without an oxygen atom in the hydrocarbon group, R' represents a trivalent hydrocarbon group having from 6 to 10 carbon atoms, and R'' represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or an alkenyl group having from 2 to 4 carbon atoms.

35 6. A process according to any of the preceding claims, wherein the hydrolysis and polycondensation is carried out using water in an amount less than 1/2 times by mole of the alkoxy groups in said organic functional group-containing alkoxy silane whereby the resultant organopolysiloxane has both the organic functional group and the alkoxy group, or in an amount of from 1/2 times to 50 times by mole of the alkoxy groups in said organic functional group-containing alkoxy silane.

40 7. A process according to any of the preceding claims, wherein a monoalkoxy silane is present at a molar ratio between said monoalkoxy silane and said organic functional group-containing alkoxy silane or said mixture of 0.01:3 to 1:3 whereby said organopolysiloxane is substantially free from any residual OH group.

45 8. A process according to any of the preceding claims, wherein said at least one compound is used in an amount of up to 99.9 wt% of the total of said organic functional group-containing alkoxy silane and said at least one compound.

50 9. A process according to any of the preceding claims, wherein said mixture comprises at least 70 wt% of tri, tetra and higher alkoxy functional group-containing compounds and the amount of water is in the range of 1 to 50 times by mole of the total alkoxy group in the mixture. whereby said organopolysiloxane is obtained in the form of a solid.

10. A process for preparing a mercapto group-containing organopolysiloxane of the following average compositional formula (1)



wherein Y^1 represents an organic group having a mercapto group, R^1 represents at least one substituted or unsubstituted monovalent hydrocarbon group having from 1 to 8 carbon atoms, R^2 represents at least one member